U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-258 753-T

Coulometric Method of Determining the Compounds in the Air Which Contain Halides

Environmental Protection Agency, Research Triangle Park, N C

1971

300045

EPA-YR 647-73 L
ARTIC 46785

MAIN ADMINISTRATION OF THE HYDROMETEOROLOGICAL SERVICE
USSR COUNCIL OF MINISTERS

PB 258 753-T

ORDER OF THE RED BANNER OF LABOR
MAIN GEOPHYSICAL OBSERVATORY imeni A. I. Boyeykov

WORKS

Issue 254

ATMOSPHERIC DIFFUSION AND AIR POLLUTION : 162-171

Edited by
Doctor of Physical-Mathematical Sciences
M. Ye. Berlyand

Hydrometeorological Press

Leningrad 1971

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

BIBLIOGRAPHIC DATA SHEET	1. Report No. EPA TR73-647L	2.	3. Recipient's Accession No.
4. Title and Subtitle: Coulometric method of determining the compounds in the air which contain halides			5. Report Date: 1971 6.
7. Author(s): N.Sh. Vol'berg			8. Performing Organization Rept. No.
9. Performing Organization Name and Address: TRANSLATED FROM RUSSIAN BY EPA			10. Project/Task/Work Unit No. 11. Contract/Grant No.
12. Sponsoring Organization Name and Address: Translation Service, Office of Administration - Library, Research Triangle Park, NC 27711			13. Type of Report & Period Covered 14.

15. Supplementary Notes

ATMOSPHERIC DIFFUSION AND AIR POLLUTION 1971, pp.162-171

16. Abstracts

17. Key Words and Document Analysis. 17a. Descriptors

EPAISD

17b. Identifiers/Open-Ended Terms

AIR POLLUTION- MEASUREMENT METHODS

17c. COSATI Field/Group 13B 68A

PRICES SUBJECT TO CHANGE

18. Availability Statement: THIS TRANSLATION WAS MADE FROM A NON-COPYRIGHTED TEXT	19. Security Class (This Report) UNCLASSIFIED	21. No. of Pages 17
	20. Security Class (This Page) UNCLASSIFIED	22. Price $3.50

FORM NTIS-35 (10-70)

USCOMM-DC 40329-P71

TR 647-73 L
APTIC 46785

COULOMETRIC METHOD OF DETERMINING THE COMPOUNDS IN THE AIR WHICH CONTAIN HALIDES

[Kylonometricheskiy metod opredeleniya galogensoderzhashchikh soyedineniy v vozdukhe]

N.Sh. Vol'berg

Atmospheric diffusion and air pollution
1971, pp. 162-171

Translated for EPA by
SCITRAN (SCIENTIFIC TRANSLATION SERVICE)
SANTA BARBARA, CALIFORNIA

COULOMETRIC METHOD OF DETERMINING THE COMPOUNDS IN THE AIR WHICH CONTAIN HALIDES

N.Sh. Vol'berg

The problem of determining the nature of the large number of harmful substances in the air by automatic means can be solved only by having a multi-purpose gas analyzer. Previously we selected conditions for coulometric determination using one device for a number of compounds containing sulfur (sulfur dioxide, hydrogen sulfide and carbon disulfide) when these occur together in the air [3]. The purpose of the present study is to develop conditions coulometric determination of the free halides and halide-containing compounds.

DETERMINATION OF FREE HALIDES

The literature describes a number of coulometric cells intended for determining the presence of chlorine and other free halides [7 - 9]. The majority are based on the continuous flow or circulation of an electrolyte. The simplicity and reliability of the cell of the non-circulating type developed for measuring sulfur dioxide [1] stimulated us to use a similar design for determining free halides. For this purpose, the sulfur dioxide cell (small model) was altered as follows. The pyrolucite electrode was replaced by an electrode made of porous silver, deposited on graphite, and the cell was filled with a different electrolyte. The gas was added to the solution by means of a slender teflon tube to avoid absorption of the halide.

The silver electrode was prepared by multiple deposition of silver nitrate crystals on the heated graphite rod by decomposition of the salt in a furnace at 600 - 800°C.

When air containing free halide enters the cell, the following reactions occur on the electrodes:

$$Cl_2 + 2e \rightarrow 2Cl^- \quad \text{and} \quad Ag - e + Cl^- \rightarrow AgCl$$

Continuous bubbling of air through the limited volume of the electrolyte in a cell of the non-circulating type can lead to rapid evaporation of the water and crystalization of the dissolved salts on the electrodes, resulting in a decrease of their transmission of current. Therefore, special emphasis was placed on developing an electrolyte for filling the coulometric cell.

It was considered necessary that the electrolyte contain compounds that prevent desiccation and promote dissolution of the free halides in the aqueous medium. The organic acids that are usually employed in such cases — glycerin, ethylene glycol, etc. — are undesirable due to the possibility of a chemical reaction. We recommend an electrolyte which is composed of a 25% solution of lithium chloride, characterized by high hygroscopicity.

To increase the solubility of the halides in the water, the iodides of alkaline metals are used which form weak complexes with precipitation of the iodide. However, the addition of iodides to the electrolyte is undesirable because it impedes the operation of the silver electrode. Therefore, the search for a complex-forming substance was conducted among organic substances.

We did not succeed in finding a complex-former directly for the chlorine, and therefore decided to use the ability of elementary bromine to form complexes, particularly with acetamide. In order to transfer the chlorine into an equivalent amount of bromine, a small amount of lithium bromide was added to the electrolyte (lithium chloride). On the basis of experiments to test the staying power of chlorine and bromine, the following composition was selected for the electrolyte: lithium chloride — 25%; lithium bromide — 0.02%; acetamide — 4%.

The solution of lithium chloride with the above-mentioned additives was tested directly in the coulometric cell. The strength of the current generated

by the cell when containing electrolytes of different composition was compared, with a constant concentration of halide in the air bubbled through the cell.

With equal amounts of chlorine and bromine, the diffusion feed [2] was used. When feeding chlorine into the ampule, the feeder was filled with a solution of chlorine in carbon tetrachloride, while — when bromine was being fed — the solution was in pure bromine. Constant feed of iodine vapor was ensured by passing air through a layer of its crystals, with the feed being limited by a very thin glass capillary. The concentration of the various halides was regulated, so that the current in the generating cell was between 30 and 40 μA. The results of the measurements that were obtained with electolytes of various compositions are shown in Table 1.

It is clear from the data which were obtained that the current yield as a function of the electrically active substance changed comparatively little for electrolytes that had different compositions. The lowest value was obtained for an electrolyte composition when iodine was being measured, which gives almost the same current yield for all solutions tested. In view of the low solubility of iodine in the solution of electrolyte, this is evidently explained by the ability of iodine to be absorbed by the electrodes, which was observed by a number of authors. Chlorine produces the maximum current yield in electrolyte 4; bromine gives approximately the same results for all electrolytes which contain acetamide.

Hence, tests in the cell confirmed the advisability of using an electrolyte with the following composition: lithium chloride - 25%; lithium bromide - 0.02%; acetamide - 4%. The background current of the cell with this electrolyte and its electrode made of gold mesh having a surface of 8 cm^2 was 0.3 μA and was performed with an error of ± 0.1 μA.

In special experiments, the optimum rate of air feed (containing chlorine) was defined. For this purpose, a constant amount of gas per unit time was added to the flow of air bubbled through the cell from a feeder, and the relationship between the magnitude of the generated current and the velocity

TABLE 1

Current Strength (μ A) as a Function of Electrolyte Composition

No. of Electrolyte	Composition of Electrolyte	Chlorine	Bromine	Iodine
1	Lithium chloride -- 25%	26.0	33.0	41.0
2	Lithium chloride -- 25%, acetamide -- 4%	28.0	43.5	42.5
3	Lithium chloride -- 25%, acetamide -- 25%	29.5	44.5	42.5
4	Lithium chloride -- 25%, acetamide -- 4%, Lithium bromide - 0.02%	30.0	45.0	41.5
5	Potassium bromide -- 3.5%, sodium iodide -- 0.075%, phosphate buffer pH 7	29.0	44.0	42.5
6	Lithium chloride -- 25%, lithium bromate -- 1%.	29.0	41.5	41.0

of the air was determined. The resultant data indicate that, in the range from 30 to 100 ml/min, the current is independent of the velocity while at higher velocities (or lower ones) it decreases insignificantly.

The output of current generated by the coulometric cell as a function of the electrically active substance passed through it was estimated by comparing it with the data from chemical analysis. For this purpose, the amount of chlorine or bromine emerging from the diffusion feeder per unit time was determined simultaneously.

Comparative experiments were performed on relatively large concentrations of substances to ensure optimum accuracy of photometric measurements: 10-40 mg/m^3 for chlorine and 2-10 mg/m^3 for bromine. The current output found in this fashion turned out to be nearly theoretical and was equal to 98 ± 2% and 94 ± 3%, respectively, at f = 9 and 5 and α = 0.95 (where f is the number of degrees freedom and α is the degree of reliability).

The results obtained indicate the possibility of using this type of cell for determining the microconcentration of chlorine without preliminary calibration.

DETERMINATION OF HYDROGEN CHLORIDE

Determination of the amount of hydrogen chloride and other halogen hydrides by the coulometric method is possible after they have been oxidized to free halide.

Studying the reaction of hydrogen chloride with various oxidizers, we concluded that the most promising method involved a reaction with potassium bromate, inasmuch as it is not accompanied by a loss of chlorine such as takes place when anoins or oxides containing metal are oxidized.

I.Ye. Tychkova and Ye.D. Filyanskaya [5], studying the properties for a number of oxidizers in conjunction with the development of a linearly coloristic method of determining HCl in air, also concluded that potassium bromate is the most suitable oxidizer for hydrogen chloride.

In order to increase the chemical activity of neutral potassium bromate, the latter (in the form of saturated solution) was placed on porous materials with more or less developed specific surface. To avoid adsorbtion of the chlorine, large-pored carriers were used. This requirement was satisfied by inert carriers intended for gas chromatography: diatomitic carrier (TND-TS-M) and hydrothermally processed silica gel with a specific surface of 70 mg^2/g — silochrome-3.

In addition to the above, we also tested porous teflon-4 which has a very low adsorptive capacity.

The oxidizers were prepared as follows. The carriers were boiled with diluted 1:1 HCl and rinsed with hot distilled water until a neutral reaction

was obtained, after which they were heated to 900°C for one hour. The necessary amount of powder (0.2-0.25 mm fraction) was heated in a drying cabinet to 100°C and mixed with an equal amount of a hot solution of potassium bromate. A weighed quantity was obtained from this calculation such that the finished product contained a dry salt that was 20% by weight. Then the powder was dried for two to three hours at 110-120°C, mixing periodically. The teflon-4 carrier was prepared as follows. The inoculated teflon powder was poured on an aluminum tray in a layer 20 mm thick, then placed for 30 minutes inside a muffle furnace heated to 380°. To avoid local overheating, the tray was placed on porcelain supports. Then the sintered mass was taken out, cut into small pieces with knives, ground in an electric coffee mill and screened to yield a fraction measuring 0.25-0.5 mm. The teflon powder was mixed with an equal volume of acetone and added to an equal volume of an aqueous solution of potassium bromate at a temperature of 30°. The potas- bromate which then precipitates out is distributed evenly into the pores of the carrier by uniform agitation. Then the preparation is mixed with an initial volume of acetone, the excess fluid is decanted, and drying is carried out first in air and then in a drying cabinet at 60°C.

Tests of various oxidizers were conducted at the given concentrations of hydrogen chloride obtained in a diffusion feeder [2].

As the source of the hydrogen chloride, we used a solution of lithium chloride in hydrochloric acid. The air was dried with a TND carrier before entering the feeder, where it was impregnated with potassium chloride or lithium chloride.

The oxidizer thus tested was placed in a vertical glass tube on a plug made of quartz glass wool. The throughput rate of the mixture of air and hydrogen chloride was 100 ml/minute. In the experiments, we measured the current strength in a coulometric cell and found it to be proportional to the amount of hydrogen chloride oxidized to free halide. The data obtained (averages from several determinations) are shown in Table 2.

TABLE 2

Influence of Carrier on the Oxidation of Hydrogen Chloride by Potassium Bromate (yield in μA)

Carrier	Volume of Oxidizer (ml)								
	0.01	0.025	0.05	0.1	0.2	0.3	0.4	0.5	1.0
Teflon - 4	-	16	22	23	26	27.4	31	31	-
TND	-	30	30	31	26.5	-	26	-	-
Silochrome - 3	28.5	28.5	28.5	29.5	29.5	-	-	29.5	30.5

The results of the measurements indicate a high oxidative activity of $KBrO_3$ deposited on silochrome-3 and TND; more than 90% of the hydrogen chloride (with a concentration on the order of 7 μg/l and a rate of 100 ml/min.) is oxidized by a layer with a total volume of 0.01 ml. Potassium bromate on teflon has less oxidizing capacity — in order to achieve total oxidation, 0.4 ml of powder are required.

When using TND as the carrier, the maximum yield of free halide is obtained with a layer volume of 0.1 ml. A further increase in the amount of oxidizer led to a decrease in the current; this is evidently explained by the interaction between the free halide and the carrier material. This undesirable phenomenon was not observed in tests using the oxidizer on the silochrome-3 carrier.

We also studied the influence of atmospheric humidity on the completeness of HCl oxidation. It was established in a series of experiments that in dry air the oxidizing activity of the layer is considerably decreased — when the amount of oxidizer is 0.3 ml, the readings in the dry air are approximately one third less than in ordinary air.

Heating the layer also decreases its oxidizing capacity. Thus, with a constant concentration of HCl, an increase in the temperature of the oxidizer

to 100°C led to a drop in the current in the coulometric cell from 155 to 80 A, i.e., the yield of chlorine dropped by approximately a factor of 2. After cooling the layer, its oxidizing capacity is completely restored, indicating the lack of decomposition. Inasmuch as the operation of the device may involve various conditions, we considered it to be highly desirable to use an oxidizer which was insensitive to temperature changes. The decrease in the activity of the oxidizer when the temperature rose even in dry air is evidently indicative of the fact that for a successful performance of the reaction the layer must contain a small amount of moisture.

To maintain sufficient humidity in the composition of the oxidizer, a hygroscopic salt (lithium chloride) was added, 1.5 and 20% by weight. The most favorable results were obtained with an oxidizer containing 5% lithium chloride. Having the same oxidizing capacity at room temperature as within LiCL, this chemosorbent changed it comparatively little when heated, even to 100°C. With an oxidizer volume of 0.3 ml, the current output fell by 8% in all, and by a factor of 2 when no lithium chloride was added.

Hence, in order to oxidize HCl when the air to be analyzed is flowing at 100 ml/minute, 0.2 ml of silochrome-3 should be used which contains 20% potassium bromate by weight and 5% lithium chloride.

The completeness of the oxidation of the hydrogen chloride under the conditions described was checked by comparing the data from the determination of the concentration of HCl in air by the chemical method (using the reaction with mercury rhodanide) and the results of the coulometric determination.

The gas mixtures were obtained dynamically and contain from 50 to 200 mg/m^3 of HCl. The current yield thus obtained was 92 ± 3.5% at f = 14 and $\alpha = 0.95$.

DETERMINATION OF CHLORINATED HYDROCARBONS

For a coulometric determination of chlorinated hydrocarbons, it was necessary first of all to develop a combustion device of small size and weight which would make it possible to transport the air to be analyzed at a rate governed by the technical data of the coulometric cell — 100 ml/minute.

In order to have maximum intensification of the process, we decided to use catalytic combustion in the presence of finely crushed platinum on the carrier. Catalysts were tested which contain various amounts of platinum on carriers with different structures. The high degree of dispersity of the platinum was achieved by reducing its chloride with a solution of ascorbic acid, neutralized with sodium carbonate. The catalysts were prepared as follows. The carrier was soaked uniformly with a solution of platinum chloride in water containing 1 or 5% platinum (converted to the metal), dried in a drying cabinet at 200°C, and boiled for 15 minutes in a small amount of 10% solution of ascorbic acid which had previously been neutralized in sodium carbonate to pH 7.

The catalyst was carefully washed with boiling distilled water (until a negative reaction was obtained to the ion of chlorine and three times more after that), then dried in a drying cabinet, and calcined at a temperature of 800° for one hour. The tests of the catalysts were conducted in a vertically mounted quartz tube 3 mm in diameter, heated by a MA-G furnace with a heating zone 50 mm long. The temperature of the furnace was measured and maintained at a set level by a ETV potentiometer. The catalyst was placed on a plug made of quartz wool inserted in the tube. The lower end of the tube containing the catalyst was connected to a cartridge containing 0.2 ml of oxidizer, connected to the coulometric cell. Air was constantly pumped through the system at the rate of 100 ml/minute.

The efficiency of the catalysts was tested with respect to the combustion of dichlorethane vapor, whose constant flow was produced by means of a

TABLE 3

Comparative Results of Tests of Various Combustion Catalysts

No.	Carrier	Specific Area (m^2/g)	Content Of Platinum (%)	Volume of Catalyst (%)	Oxidized Dichlorethane (%) at Temperature °C			
					900	800	700	600
1	Empty tube	-	-	-	88	38.3	0	-
2	-	-	99.9	Pt screen 4.5 cm^2	95	67		
3	Silochrome-1	26	5	0.05	100	100	98	
4	Silochrome-3	70	1	0.05	100	95	57	
5	INZ-600	≈40	5	0.05	100	89		
6	Chromosorb	1-2	1	0.05	100	95	60	
7	Silica gel	346	1	0.025		91	73	
				0.05	100	100	97	85
				0.1		100	99	92
8	Aluminum oxide . . .	Not Known	5	0.05	100	100	100	100

NOTE: Experimental conditions: tube diameter -- 2.6 mm; air throughput rate -- 0.1 liters/minute; dichlorethane concentration -- 10 mg/m^3.

diffusion feeder [2]. In the experiments, the current of the coulometric cell generated during passage of chlorine into it was measured, as was the product of the catalytic combustion of dichlorethane (hydrogen chloride) formed during oxidation of the product. Table 3 shows the value of this current with respect to the current of the coulometric cell during combustion of dichlorethane in an empty quartz tube 6 mm in diameter, taken as 100%. This latter procedure was performed in a furnace with a heating zone length of 190 mm at 900° and an air throughput rate of 30 ml/minute.

It is clear from the data presented in the Table that at 900° all of the tested catalysts based on dispersed platinum ensure combustion of the dichlorethane even at layer volume of 0.05 ml; at 700° — silica gel with a small specific surface but with a high content of platinum — 5%, and silica gel with a relatively large specific surface — 346 m^2/g. A particularly high oxidizing capacity is exhibited by platinum which is deposted on aluminum oxide which

provides quantitative combustion even at 600°. However, the slow rate of desorption of the hydrogen chloride which is formed makes it disadvantageous to use.

Hence, on the basis of the experiments that have been performed, it is recommended that the combustion catalyst that is used be platinized large-pored silica gel (specific surface 300-400 m^2/g), containing at least 1% platinum in a layer 0.1 ml thick and at 700°.

After seeking the optimum conditions for catalytic combustion of dichlorethane, the oxidation of the hydrogen chloride which is formed and the coulometric determination of the free halide, the method was tested as a whole at the given concentrations of dichlorethane.

In order to obtain continuously the exactly known small concentrations of vapor of volatile liquid, a diffusion feeder was devised with an optical consumption measuring system [4].

In a statistical analysis of the measurement results, it was found that in a range of concentrations from 2 to 37 mg/m^3 the output current is 95% of the theoretical value with a probable square deviation of the mean arithmetic (for $\alpha = 0.95$) of $\pm$ 2.2% at $f = 17$. In determining very small concentrations of vapor on the order of 0.4 mg/m^3, the current output fell to 80%.

Later we tested the possibility of determining other chlorated hydrocarbons by means of the method described. On the basis of the experiments that were performed, it was found that methylene chloride gives a current yield which is 82% of the theoretical value; chloroform yields 92%. Carbon tetrachloride is not oxidized under the conditions selected.

Inasmuch as the coulometric determination of chlorinated hydrocarbons destroys chlorine and hydrogen chloride, we tested a number of sorbents to absorb them. The best results were shown by potassium carbonate together

with sodium thiosulfate applied to the inert porous carrier known as TND (sperochrome-1) and stained with phenolphthalein. The sorbent effectively inhibits the chlorine and hydrogen chloride without absorbing the vapors of the highly volatile chlorinated hydrocarbons. The sorbent is replaced as it is used up.

Hence, on the basis of the studies that were performed, a coulometric method of determination of various chlorine-containing substances in air was devised. In theory, the method may be viewed as a general one for the determination of chlorine in organic compounds (not perchlorinated), but some deviations in the current yield from the theoretical value are observed, and indicate the necessity for experimental testing in each individual case.

The results that were obtained were used as the basis for designing a working model of the automatic gas analyzer to determine free halides, hydrogen chloride, and chlorinated hydrocarbons. In determining chlorine, the air to be analyzed is fed continuously into the coulometric cell, while in the case of hydrogen chloride determination it is passed beforehand through a tube containing an oxidizer, silochrome-3 containing 20% potassium bromate, and 5% lithium chloride. The chlorinated hydrocarbons are determined following combustion on platinized large-pored silica gel at 700-800°C and oxidation by potassium bromate. To remove the chlorine and hydrogen chloride in determining the chlorinated hydrocarbons, a cartridge is used containing a mixture of potassium carbonate and sodium thiosulfate, applied to a porous carrier.

At a flow rate of air to be analyzed of 0.1 l/min. and the use of a second instrument with a 0-5 μA scale, the gas analyzer described gives a sensitivity on the order of tenth of a milligram for a m^3 of air and a lag time of 10-15 minutes.

In summarizing the above, we can see that the use of a preliminary reaction with solid sorbents and catalysts is a very promising method for the development of multipurpose gas analyzers for continuous operation. An advantage of such devices in comparison with other known multipurpose gas analyzers —

for example, photocolorimetric ones — is the possibility of achieving a rapid transition from measurement of one compound to measurement of another by a simple turn of a multishift gas cock.

REFERENCES

1. Al'perin, V.Z. et al. An Improved Galvanic Coulomb-Polarigraphic Cell for Measuring Concentration of Sulfur Dioxide. In the book: Avtomatizatsiya Khimicheskikh Proizvodstv (Automation of Chemical Production). First edition. Moscow, 1968, pp. 76-82.

2. Vol'berg, N.Sh. Device for Dynamic Transmission of Small Amounts of Gases and Vapors into a Flow of Air. In the book: Metody Opredeleniya Vrednykh Veshchestv v Vozdukhe (Methods of Determining the Amount of Harmful Substances in Air). Leningrad, 1968, pp. 130-134.

3. Vol'berg, N.Sh. The Coulometric Method of Determining Sulfur-Containing Compounds in Air. Trudy GGO, No. 238, 1969, pp. 107-114.

4. Vol'berg, N.Sh. A Feed Device for Vapors of Volatile Liquids. Trudy GGO, No. 238, 1969, pp. 229-231.

5. Tychkova, I.Ye. and Ye.D. Filyanskaya. The Linear-Coloristic Method of Determination of Hydrogen Chloride. Trudy VNIIOT, 1967, p. 280.

6. Dubois, L., A. Zdrojewski and Monkman. The Analysis of Carbon Monoxide in Urban Air at the ppm Level, and the Normal Carbon Monoxide Value. J. Air Poll. Control Ass., Vol. 16, No. 3, 1966, pp. 135-140.

7. Ersepke, Z. and J. Baranek. A Device for Analyzing the Amount of Chlorine in Air. Chem. Průmysl, Vol. 16, No. 8, 1966, pp. 496-497.

8. Soucek, J. Coulometric Determination of Chlorine in Gases. Chem. Průmysl, Vol. 13, 1963, pp. 470-471.

9. Waclawik, J. and S. Waszak. A Method of Determining Small Amounts of Chlorine in Gases. Chem. analit. (Polska), Vol. 12, 1967, pp. 877-883.